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(54) SPRAYED COATING STRUCTURE

(57)Abstract:
PURPOSE: To suppress the abnormal oxidation of a base coating layer and to effectively prevent the peeling of a thermal shielding layer by using a Co-Ni-Cr- Al alloy added with Hf as the base coating layer.
CONSTITUTION: On the surface of a metallic base metal, a base coating layer constituted of a Co base alloy contg., by weight, 5 to 15% Ni, 10 to 25% Cr, 5 to 15% Al and 0.5 to 2.5% Hf is formed by thermal spraying. Its surface is thermal-sprayed with oxide ceramics or cermet contg. ≥50vol.% oxide ceramics to form a shielding coating layer. In this way, the protective oxide film formed of Cr and Al is strengthened, by which the abnormal oxidation of the base coating layer is suppressed even under severe using conditions to improve the adhesion of the thermal shielding layer as the upper layer.

CLAIMS

[Claim(s)]
[Claim 1] Flame-spraying structure characterized by consisting of a Co radical alloy with which it has the substrate enveloping layer which carried out thermal spraying of the metal and formed it on the metal base material, and the thermal insulation enveloping layer which carried out thermal spraying of the cermet which contains oxide ceramics or oxide ceramics more than 50 volume %, and formed it on it, and

said substrate enveloping layer contains nickel:5-15%, Cr:10-25%, aluminum:5-15%, and Hf:0.5-2.5% by weight %.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the flame-spraying structure of using in order to give thermal resistance to metal components, such as a roll in a heat treating furnace.
[0002]
[Description of the Prior Art] In order to raise conventionally the thermal resistance of the metal components with which the thermal resistance of the roll in a heat treating furnace etc. is demanded, carrying out flame spraying of the cermet which contains oxide ceramics or oxide ceramics more than 50 volume % as a thermal insulation layer on a metal base material is performed. However, since the thermal insulation enveloping layer has the low adhesion over a metal base material, it has been usually to make the substrate enveloping layer by metallizing intervene between a metal base material and a thermal insulation enveloping layer.
[0003] As an ingredient of this substrate enveloping layer, the heat-resistant alloy of nickel radical which contained Cr and aluminum so much, or Co radical is used abundantly. However, when pore exists in the thermal insulation enveloping layer which consists of oxide ceramics or a cermet and a substrate enveloping layer consists of said heat-resistant alloy, under an elevated temperature, oxidation of a substrate enveloping layer progresses through the pore of a thermal insulation enveloping layer. Consequently, adhesion may fall on the boundary of a thermal insulation enveloping layer and a substrate enveloping layer, and a thermal insulation enveloping layer may exfoliate from a boundary.
[0004] as one of the cure of this -- "-- using low pressure plasma spraying for a bonding coat is indicated by elevated-temperature society magazine 217th page - 226th page". [of volume / 15th / the 5 No. (September, 1989)]
[0005]
[Problem(s) to be Solved by the Invention] If low pressure plasma spraying is used as a bonding coat of the thermal insulation enveloping layer which consists of oxide ceramics or a cermet, a precise substrate enveloping layer will be formed. Although this substrate enveloping layer oxidizes through the pore of a thermal insulation enveloping layer at the beginning, since it functions as a protective layer precise [the formed oxidizing zone] and powerful, too much oxidation does not take place, consequently exfoliation of a thermal insulation enveloping layer is prevented.
[0006] However, as compared with a usual plasma metal spray, usual oxy fuel spraying, etc. which are performed in atmospheric air, a facility becomes large-scale, and workability is also remarkably inferior in low pressure plasma spraying.
[0007] Also when the usual spraying process is used, the catastrophic oxidation of the substrate enveloping layer which let the thermal insulation enveloping layer pass is controlled, and the purpose of this invention is to offer the flame-spraying structure where exfoliation of a thermal shield layer is prevented effectively.
[0008]
[Means for Solving the Problem] The flame-spraying structure of this invention has the substrate enveloping layer which carried out thermal spraying of the metal and

formed it on the metal base material, and the thermal insulation enveloping layer which carried out thermal spraying of the cermet which contains oxide ceramics or oxide ceramics more than 50 volume %, and formed it on it, and is characterized by to consist of a Co radical alloy with which said substrate enveloping layer contains nickel:5-15%, Cr:10-25%, aluminum:5-15%, and Hf:0.5-2.5% by weight %.
[0009] That is, the flame-spraying structure of this invention uses a Co-nickel-Cr-aluminum-Hf alloy for a substrate enveloping layer, and is characterized [greatest] especially by addition of Hf.
[0010] Generally this kind of alloy is called a M-Cr-aluminum-X alloy, and is used as a bonding coat of ceramic thermal spraying. Here, as for M, nickel, Co, or a nickel-Co alloy is used by the base element. And compound addition of Cr and the aluminum is carried out at this base element, a protection nature oxide film is formed in the front face of a substrate enveloping layer, and the element X for reinforcing this protection nature oxide film is added further. As this element, Y is usually used. However, when a spraying process is a plasma metal spray, oxy fuel spraying, etc. which are performed in atmospheric air, and when a service condition is cruel, the catastrophic oxidation of the substrate enveloping layer which let the upper thermal insulation enveloping layer pass is not fully controlled, but the upper exfoliation arises at an early stage comparatively.
[0011] The protection nature oxide film which replaces the flame-spraying structure of this invention with Y, and Cr and aluminum form by this using Hf is strengthened remarkably, also under a severe service condition, the catastrophic oxidation of a substrate enveloping layer is controlled and the adhesion of the upper thermal insulation enveloping layer is improved sharply.
[0012]
[Function] In the flame-spraying structure of this invention, a thermal insulation enveloping layer is based on oxide ceramics or a cermet, and is constituted. As oxide ceramics, aluminum 2O3 excellent in thermal resistance, TiO2, Cr 2O3, SiO2, ZrO2, CaO, Y2 O3, MgO(s), these multiple oxides, etc. can be mentioned. A cermet shall contain these oxide ceramics more than 50 volume %. Since thermal insulation nature becomes precise [a thermal insulation enveloping layer] low and oxidation of the substrate enveloping layer which let this pass does not pose a big problem when the ratio of oxide ceramics is under 50 volume %, this is taken as the outside of an object. The heat-resistant alloy which usually used nickel, Co, or a nickel-Co alloy as the base is used for the remaining metals.
[0013] A substrate enveloping layer is taken as Co radical alloy which contains nickel:5-15%, Cr:10-25%, aluminum:5-15%, and Hf:0.5-2.5% by weight %.
[0014] It combines with a metal base material in metallurgy, and Co which is a base element does so the effectiveness which raises adhesion with a metal base material while contributing to reservation of the high temperature strength of a substrate enveloping layer.
[0015] nickel does so the same effectiveness as Co. That is, the high temperature strength of a substrate enveloping layer and adhesion with a metal base material improve by adding nickel of the specified quantity to Co. The effectiveness is acquired in the range whose amount of nickel is 5 - 15%.
[0016] Cr is the element which gives oxidation resistance, forms the oxide film excellent in protection nature in the front face of a substrate enveloping layer, and suppresses advance of oxidation inside. Since the effectiveness will cause embrittlement if it exceeds 25% although it shows up at 10% or more, the amount of Cr(s) is made into 10 - 25%.

[0017] aluminum forms a protection nature oxide film in the front face of a substrate enveloping layer as well as Cr, and stabilizes a substrate enveloping layer by coexisting with Cr. The effectiveness shows up in the range whose amount of aluminum is 5 - 15%.
[0018] Hf is the element by which it is characterized [of this invention], and when added by the above-mentioned Co-nickel-Cr-aluminum alloy, it strengthens the protection nature oxide film which Cr and aluminum form. That is, the adhesion of a thermal insulation enveloping layer is raised by raising the chemical stability in the elevated temperature of the protection nature oxide film formed in the front face of a substrate enveloping layer, and suppressing advance of oxidation. Since the effectiveness will cause embrittlement if it exceeds 2.5% although it shows up at 0.5% or more, the amount of Hf(s) is made into 0.5 - 2.5%.
[0019] Even if a plasma metal spray, oxy fuel spraying, etc. which are performed in atmospheric air as a spraying process are used for the flame-spraying structure of this invention of having such a substrate enveloping layer, it does not have the catastrophic oxidation of the substrate enveloping layer which let the upper thermal insulation enveloping layer pass under the elevated temperature, and cannot produce exfoliation of a thermal insulation enveloping layer easily. That is, since oxidation starts only on the front face of a substrate enveloping layer and the oxide film turns into powerful protection sex skin film, advance of future oxidation is prevented and exfoliation of the upper thermal insulation enveloping layer is prevented by maintaining the function of a substrate enveloping layer for a long period of time.
[0020]
[Example] The example of this invention is explained below.
[0021] Substrate covering of the furring shown in Table 1 on the front face of the metal base material which consists of SUS310S (5mm thickness x50mm angle) was carried out at the thickness of 0.1mm by low pressure plasma spraying and the atmospheric-air plasma metal spray. Furthermore, the atmospheric-air plasma metal spray of the oxide ceramics and the cermet which are shown in Table 2 was carried out to the front face of each substrate enveloping layer, and the thermal insulation enveloping layer of 0.3mm thickness was formed in it.
[0022] It is JIS about the obtained sample. The heating friction test of H8666 (ceramic thermal-spraying test method) was presented. It was 1000 degrees C, and whenever [stoving temperature] measured the number of heat cycles until exfoliation of a thermal insulation enveloping layer starts a maximum of 50 times, and evaluated the adhesion at the time of the heating at high temperature. A result is shown in Table 3.
[0023]
[Table 1]

下地被覆層の組成（ｗｔ％）

No.	Ｎｉ	Ｃｒ	Ａｌ	Ｈｆ	Ｙ	Ｃｏ	区　分
1	7	23	12	——	——	Bal.	比　較　例
2	〃	〃	〃	——	0.8	〃	〃
3	〃	〃	〃	0.3	——	〃	〃
4	〃	〃	〃	0.5	——	〃	本発明例
5	〃	〃	〃	1.0	——	〃	〃
6	〃	〃	〃	2.0	——	〃	〃
7	〃	〃	〃	2.5	——	〃	〃
8	〃	〃	〃	3.0	——	〃	比　較　例

[0024]
[Table 2]

遮熱被覆層の組成

	ZrO_2・8 %Y_2O_3	Co-7%Ni -23%Cr -12%Al-0.8%Y
セラミックス	100 体積%	——
サーメット	55 体積%	45体積%

[0025]
[Table 3]

下地No	セラミックス		サーメット		区　分
	減圧プラズマ	大気プラズマ	減圧プラズマ	大気プラズマ	
1	41	32	43	36	比較例
2	50	41	50	46	〃
3	45	39	50	44	〃
4	50	50	50	50	本発明例
5	50	50	50	50	〃
6	50	50	50	50	〃
7	50	50	50	50	〃
8	50	42	50	46	比較例

[0026] When the presentation of a substrate enveloping layer is No.1 (i.e., when the strengthening element of a protection nature oxide film is not included), even if it uses low pressure plasma spraying for formation of a substrate enveloping layer, the number of heat cycles until exfoliation of a thermal insulation enveloping layer starts does not become the count of the highest (50 times). Although it will become the count of the highest in low pressure plasma spraying if Y is used as this strengthening element, the count of the highest is not become in an atmospheric-air plasma metal spray (No.2). However, when Hf of optimum dose is used, also in the case of an atmospheric-air plasma metal spray, the number of heat cycles reaches at the count of the highest, and it turns out [of the effectiveness by Hf] that it is large (No.4-7).
[0027]
[Effect of the Invention] Also when atmospheric-air thermal spraying is used for the formation by using for a substrate enveloping layer the Co-nickel-Cr-aluminum alloy which added Hf, the flame-spraying structure of this invention can suppress exfoliation of the upper thermal insulation enveloping layer effectively, so that clearly from the above explanation. Therefore, thermal-spraying construction can be simplified and big effectiveness is done so to the improvement in construction efficiency. Moreover, it cannot be overemphasized that the effectiveness of protecting a metal base material is also large.

TECHNICAL FIELD

[Industrial Application] This invention relates to the flame-spraying structure of using in order to give thermal resistance to metal components, such as a roll in a heat treating furnace.

PRIOR ART

[Description of the Prior Art] In order to raise conventionally the thermal resistance of the metal components with which the thermal resistance of the roll in a heat treating furnace etc. is demanded, carrying out flame spraying of the cermet which contains oxide ceramics or oxide ceramics more than 50 volume % as a thermal insulation layer on a metal base material is performed. However, since the thermal insulation enveloping layer has the low adhesion over a metal base material, it has been usually to make the substrate enveloping layer by metallizing intervene between a metal base material and a thermal insulation enveloping layer.

[0003] As an ingredient of this substrate enveloping layer, the heat-resistant alloy of nickel radical which contained Cr and aluminum so much, or Co radical is used abundantly. However, when pore exists in the thermal insulation enveloping layer which consists of oxide ceramics or a cermet and a substrate enveloping layer consists of said heat-resistant alloy, under an elevated temperature, oxidation of a substrate enveloping layer progresses through the pore of a thermal insulation enveloping layer. Consequently, adhesion may fall on the boundary of a thermal insulation enveloping layer and a substrate enveloping layer, and a thermal insulation enveloping layer may exfoliate from a boundary.

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EFFECT OF THE INVENTION

[Effect of the Invention] Also when atmospheric-air thermal spraying is used for the formation by using for a substrate enveloping layer the Co-nickel-Cr-aluminum alloy which added Hf, the flame-spraying structure of this invention can suppress exfoliation of the upper thermal insulation enveloping layer effectively, so that clearly from the above explanation. Therefore, thermal-spraying construction can be simplified and big effectiveness is done so to the improvement in construction efficiency. Moreover, it cannot be overemphasized that the effectiveness of protecting a metal base material is also large.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] If low pressure plasma spraying is used as a bonding coat of the thermal insulation enveloping layer which consists of oxide ceramics or a cermet, a precise substrate enveloping layer will be formed. Although this substrate enveloping layer oxidizes through the pore of a thermal insulation enveloping layer at the beginning, since it functions as a protective layer precise [the formed oxidizing zone] and powerful, too much oxidation does not take place, consequently exfoliation of a thermal insulation enveloping layer is prevented.

[0006] However, as compared with a usual plasma metal spray, usual oxy fuel spraying, etc. which are performed in atmospheric air, a facility becomes large-scale, and workability is also remarkably inferior in low pressure plasma spraying.

[0007] Also when the usual spraying process is used, the catastrophic oxidation of the

substrate enveloping layer which let the thermal insulation enveloping layer pass is controlled, and the purpose of this invention is to offer the flame-spraying structure where exfoliation of a thermal shield layer is prevented effectively.
[0008]

MEANS

[Means for Solving the Problem] The flame-spraying structure of this invention has the substrate enveloping layer which carried out thermal spraying of the metal and formed it on the metal base material, and the thermal insulation enveloping layer which carried out thermal spraying of the cermet which contains oxide ceramics or oxide ceramics more than 50 volume %, and formed it on it, and is characterized by to consist of a Co radical alloy with which said substrate enveloping layer contains nickel:5-15%, Cr:10-25%, aluminum:5-15%, and Hf:0.5-2.5% by weight %.
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OPERATION

[Function] In the flame-spraying structure of this invention, a thermal insulation enveloping layer is based on oxide ceramics or a cermet, and is constituted. As oxide ceramics, aluminum 2O3 excellent in thermal resistance, TiO2, Cr 2O3, SiO2, ZrO2, CaO, Y2 O3, MgO(s), these multiple oxides, etc. can be mentioned. A cermet shall contain these oxide ceramics more than 50 volume %. Since thermal insulation nature becomes precise [a thermal insulation enveloping layer] low and oxidation of the substrate enveloping layer which let this pass does not pose a big problem when the ratio of oxide ceramics is under 50 volume %, this is taken as the outside of an object. The heat-resistant alloy which usually used nickel, Co, or a nickel-Co alloy as the base is used for the remaining metals.
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